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Concentration of rare-earth elements by sorption from sulphate solutions

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Abstract. Constantly increasing demand for rare-earth elements contributes to the involvement in the production of ore processing waste, the content of not extracted REE in which is quite large. One of the types of such waste is man-made mineral formations from the processing of phosphate uranium ores, which serve as raw materials for the production of REE concentrate at SARECO LLP. The technology for producing a concentrate includes the following redistribution: opening of raw materials cleaning of productive solutions from impurities; obtaining a concentrate on rare earth elements. One of the main disadvantages of this technology is the coprecipitation of almost 30% REE with ferrous cake when cleaning the most productive solution from impurities. To extract the rare earth elements ferrous cake is leached with sulphuric acid. The article studies the process of sorption from both model solutions that are similar in composition to the productive leaching of ferrous cake and directly from the productive ones, with the aim of further combining the resulting eluates with solutions supplied to precipitate REE.. Considerable attention has been paid to disrupt by ammonium salts.

Key words: rare-earth elements, technogenic mineral formations (TMF), ferrous cake, sorption, desorption.

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Introduction

In connection with the recently increased demand for rare-earth elements, one of the urgent problems is the expansion of the list of raw materials that can be used as feedstock. The question of the use of waste production of rare and rare earth elements containing fairly high concentrations of unrefined REEs is being considered. One type of such waste is man-made mineral formations (TMF) from the processing of phosphate uranium ores, the content of which is the amount of REE is 5.0%.

Currently, REE concentrate is obtained from this raw material at SARECO LLP [1]. In the process of cleaning productive solutions obtained by leaching the raw material, ferrous cake is formed, with which a significant amount (up to 30%) of rare-earth elements co-precipitates. Ferrous cake is leached twice with sulphuric acid to further extract REE. The consequence of combining the obtained solutions with the productive one after purification from impurities is an increase in the cost of oxalic acid for precipitating REE concentrate. When combining these solutions with the original producers - the material flows entering the filtering increase, which complicates the already problematic filtering unit. In this regard, we have studied the method of pre-concentration of rare-earth elements by sorption from solutions of leaching of ferrous cake.

Research methodology

The model solutions with La concentration - 0.75 g/dm^3 (solution No. 1), model with concentration, mg/dm^3 were used as initial solutions: La - 98.2; Y - 89.6; Dy –58.0; Fe^{3+} - 101.4 (solution No. 2) And leaching yielding ferrous cake of the following composition, mg/dm^3: La - 98.2; Ce - 103.1; Dy –58.0; Er - 27.2; Eu — 3.9; Gd - 65.4; Ho - 13.1; Lu, 5.1; Nd, 132.1; PR — 41.3; Sm - 34.6; Tb - 9.9; Tm -4.7; Y - 89.6; Yb -26.6; $\sum$ REE - 712.8; Fe^{3+} - 4.01 g/dm^3. When the ferric iron is reduced to the divalent state, according to the method [2], its concentration in the productive solution decreases and amounts to Fe^{3+} - 101.4 mg/dm^3.

Sorption of lanthanum from model solutions was carried out in a static mode with the ratio S: L = 1: 500 for 8 hours, and productive in dynamic conditions in a 25 cm^3 column at a speed of 50 cm^3 / hour. In the course of the research, Sorbents KU-2-8n, C-100 “Purolite”, Lewatit S1567, MTC-1600 “Purolite” were used. Rare-earth elements from the resin phase were eluted with ammonium sulphate and ammonium nitrate solutions in a static mode at an S: L ratio = 1: 50.

Methods of analysis

The quantitative content of rare-earth elements was determined on an atomic emission spectrometer with an inductively coupled plasma Optima 8300DV.

The results of researches

At the first stage, experiments were carried out on the sorption extraction of lanthanum (solution No. 1) From the model solution in order to select an ion exchange for subsequent studies. The results are shown in Figure 1, from which it can be seen that REE is more actively used from ion exchangers used, for example, lanthanum, absorbs KU-2-8n sulfo cation exchange. In subsequent studies, sulfonic cation exchange KU-2-8n was used for the sorption of REE.

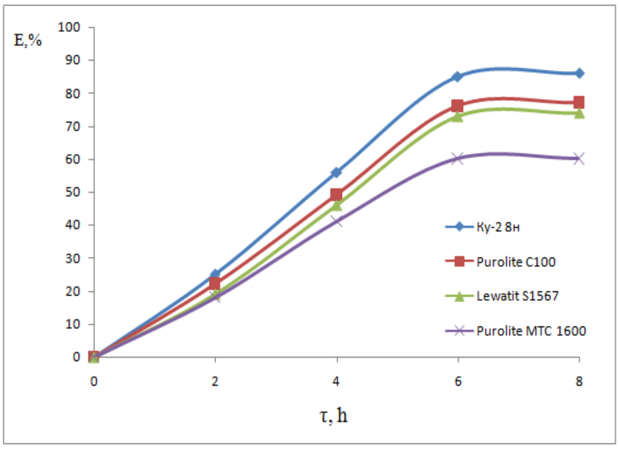

Figure 1 Lanthanum sorption from model solutions

From literary sources and our own experience it is known that ferric ions are the most negatively affected by the process of sorption of rare earth elements. Earlier, we studied the behaviour of iron and its influence on the sorption of REE in binary systems Ln^{3+} - Fe^{3+} [3] with the same concentration of components. Considering that ferric iron is the main impurity in productive solutions from leaching of ferrous cake, we investigated its effect on the REE sorption from the model solution (solution No. 2), in which the concentration of rare-earth elements correlates with the concentration in the productive ones. The content of ferric iron, as indicated above, in the model solution is equal to its residual concentration in the productive solution after reduction to the bivalent state. The rare-earth elements in the model solution are represented by lanthanum, dysprosium and yttrium. Lanthanum and dysprosium were selected as typical representatives of the subgroups of light and heavy REE, and yttrium, as a specific representative of rare-earth metals, having no f-orbits. Sorption was carried out in static conditions, according to the method indicated above. Kinetic sorption curves are presented in Figure 2.

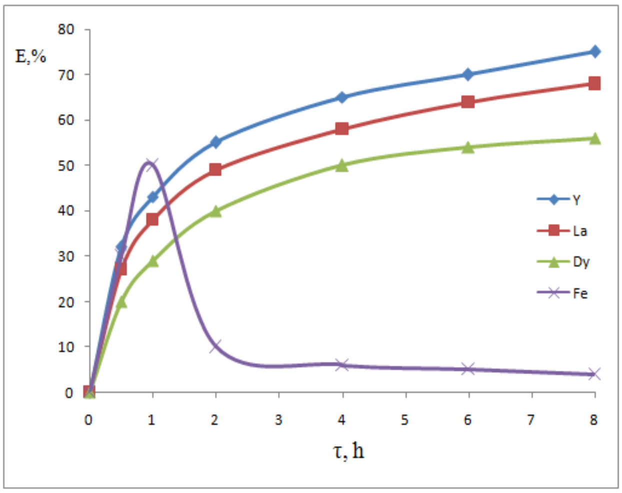

Figure 2 Sorption of rare-earth elements and iron from model solutions

As follows from the figure, the degree of sorption of rare earth elements gradually increases with time and decreases in the series Y – La – Dy. This dependence is associated with the magnitude of the ionic radius of rare-earth elements and their concentration. Iron during the first hour of the process is actively sorbed by the cationite, during the next two hours the speed of the process decreases sharply and remains almost constant. Thus, during the sorption of rare-earth elements in the presence of iron, the latter is actively sorbed at the beginning of the process, then the rate of sorption of rare-earth elements, which displace iron, increases. The process of ion exchange is characteristic not only for sorption, but also desorption. In the literature, there is information about the desorption of rare earth elements by acids, salts, compounds, forming complexes with REE [4-7]. Previously, we studied the desorption process with sulphuric acid; it was shown that elution of rare-earth elements proceeds quite effectively with sulphuric acid with a concentration of 200 g/dm^3. However, ammonium salts are of particular interest as eluates. In the literature, this issue gives considerable attention. For example, there is an ambiguous opinion regarding the use of ammonium sulphate. In literature [8], data on the study of the possibility of using $(NH_4)_2SO_4$ for desorption of lanthanides are given. It has been established that extraction of REE from the phase of cation exchanger KU-2-8n with a solution containing 30 wt. % $(NH_4)_2SO_4$, under dynamic conditions, is very effective. The degree of desorption of the sum of REEs in the described experiments reaches 87.1%. Other authors [9] indicate the difficulty of elution of REE with ammonium sulphate. The difficulties are due to the characteristic feature of the sulphates of rare-earth elements to form metastable supersaturated solutions. Equilibrium in such systems can occur for a long time and is described by the following equation:

$$2Ln^{3+}+3SO_4^{2-}\leftrightarrow Ln_2(SO_4)_3\leftrightarrow Ln(SO_4)_2^{-}+LnSO_4^{+}$$

The concentration shift of other ions in the solution certainly affects the equilibrium shift. For example, the presence of NH_4^+ ions lowers the solubility of the resulting REE sulphates. In the resulting eluates, the source authors of references [9, 12] observed the formation of precipitates of the composition $Ln_2(SO_4)_3 \cdot 8H_2O$. At a high concentration of eluent, crystallization began already in the layer of cation exchange, which made the desorption process difficult.

At this stage, we investigated the possibility of desorption of rare-earth elements by ammonium salts - sulphate and nitrate. To study the desorption process, the KU-2-8N ion exchange was pre-saturated with lanthanum from model solution No. 1. The content of lanthanum in the resin was 0.0027 Mol/g.

Further, a series of experiments on the desorption of lanthanum with ammonium sulphate solutions of different concentrations (g/dm^3: 100, 200, 250, 300, 400) was carried out. Elution was carried out in a static mode, with a ratio of S: L = 1:50, room temperature and contact time of 120 minutes.

The obtained solutions after desorption were very unstable. The formation of fine crystalline precipitation was observed. An unequivocal conclusion was made about the unacceptability of using ammonium sulphate as eluent of rare-earth elements. Ammonium nitrate desorption was studied under conditions similar to ammonium sulphate. Figure 3 shows the dependence of the degree of elution of lanthanum on the concentration of ammonium nitrate.

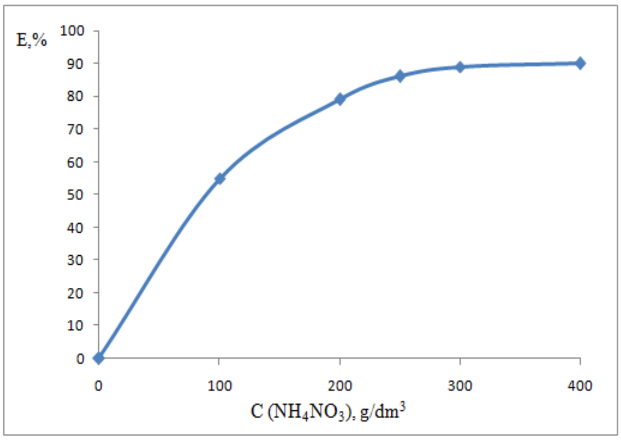

Figure 3 Dependence of changes in the degree of elution of lanthanum on the concentration of ammonium nitrate

From the figure it follows that the value of the degree of elution of lanthanum increases sharply with an eluent concentration of 300 g/dm^3 and then varies slightly, desorption with ammonium nitrate is advisable to keep the solution with a concentration of 300 g/dm^3. Further, in the course of research, the dependence of the degree of elution of REE, using lanthanum, as an example, from the cation exchange KU-2-8-n solution of ammonium nitrate with a concentration of 300 g/dm^3 on the phase contact time was studied. The results are presented in Figure 4.

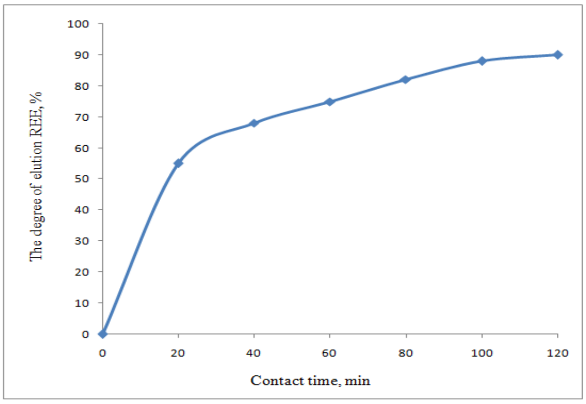

Figure 4 Change in the degree of elution of lanthanum from the phase of cation exchanger KU-2-8-n in time

Thus, from the conducted studies and the obtained results, it follows that the REE sulfonic cation exchange KU-2-8n absorbs most effectively from the tested ion exchangers. It is advisable to conduct the elution from the sulfocationite phase with a solution of ammonium nitrate with a concentration of 300 g/dm^3. The sorption rate of individual REEs depends on both their ionic radius and concentration.

Conclusions

In order to determine the prospects of sorption concentration of rare-earth elements from solutions from leaching of ferrous cake, in the first stage, the ion exchange was chosen for REE sorption. The study of the sorption of lanthanum ionites KU-2-8n, C-100 "Purolite", Lewatit S 1567, MTC-1600 "Purolite" found that the lanthanum suffocation exchange KU-2-8n was more efficiently absorbed among the studied. The study of sorption from a model solution, in which the content of individual REE and iron correlates with the productive one, showed a decrease in the degree of sorption in the series Y-La-Dy, which is associated with the ionic radius of rare-earth elements and their concentration. The iron present in the solution is actively sorbed at the beginning of the process (it can give figures from and to), then the rate of sorption of REE, which displace iron, increases.

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Күкірт қышқылды ерітінділерден, сирек кездесетін элементтерді сорбциямен концентрлеу

Кенжалиев Б. К., Суркова Т.Ю., Есімова Д.М.

Түйіндеме. Сирек кездесетін элементтер сұранысының куннен-кунге өсуі, кен қалдықтарын қайта өңдеу өндірісіне мүмкіндік береді, демек бөлінбеген СКЭ үлестері анағұрлым жоғары. Осындай қалдықтардың біріне, фосфатты уран кендерін қайта өңдегенде пайда болатын техногенді минеральды түзілімдер (ТМТ), яғни бастапқы шикізат ретінде «SARECO» ТОО-ғы СКЭ концентратын алу жатады. Концентрат алудың технологиясы, келесідей: бастапқы шикізатты ашу; өнімді ерітінділерді кірмелерден тазалау; сиреккездесетін элементтердің концентрациясын алу бөлімдерінен тұрады. Бұл технологияның негізгі кемшіліктерінің бірі, кірмелерден өнімді ерітіндіні тазартқан кезде темірлі кекпен бірге 30 % бірге шөгіледі. Сирек кездесетін элементтерді қайтадан бөліп алған жағдайда, темірлі кекті күкірт қышқылымен шаймалайды. Мақалада, СКЭ концентратын тұндыруға жөнелтетін, әрі арықарай ерітіндімен бірге элюаттарды алу мақсатында, темірлі кекті шаймалағандағы өнімнің құрамына жақын модельді ерітіндімен және тікелей өнімнің сорбциялық үрдісі зерттелінді. Десорбцияда, аммоний тұздарына аса көңіл бөлінді.

Түйінді сөздер: сирек кездесетін элементтер, техногенді минералды түзілімдер (ТМТ), темірлі кек, сорбция, десорбция.

Концентрирование редкоземельных элементов сорбцией из сернокислых растворов

Кенжалиев Б. К., Суркова Т.Ю., Есимова Д.М.

Аннотация. Постоянно увеличивающийся спрос на редкоземельные элементы способствует вовлечению в производство отходов переработки руд, содержание не извлеченных РЗЭ в которых достаточно велико. Одним из видов таких отходов являются техногенные минеральные образования от переработки фосфатных урановых руд, которые служат исходным сырьем для получения концентрата РЗЭ на ТОО «SARECO». Технология получения концентрата включает следующие переделы: вскрытие исходного сырья; очистка продуктивных растворов от примесей; получение концентрата редкоземельных элементов. Одним из основных недостатков данной технологии является соосаждение почти 30% РЗЭ с железистым кеком при очистке продуктивного раствора от примесей. Для доизвлечения редкоземельных элементов железистый кек выщелачивают серной кислотой. В статье изучен процесс сорбции как из модельных растворов, близких по составу продуктивным от выщелачивания железистого кека так и непосредственно из продуктивных, с целью дальнейшего объединения получаемых элюатов с растворами, поступающими на осаждение концентрата РЗЭ. Уделено значительное внимание десорбции солями аммония.

Ключевые слова: редкоземельные элементы, техногенные минеральные образования (ТМО), железистый кек, сорбция, десорбция.

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